

Protonation Constants for Triarylphosphines in Aqueous Acetonitrile Solutions

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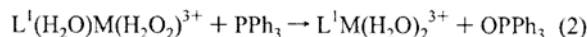
Two independent methods were used to determine protonation constants K_H for triarylphosphines in mixed acetonitrile/water media. One method is based on ^{31}P chemical shifts, and the other on the kinetics of debromination of a vicinal dibromide. The protonation constants obtained by the two methods agree well with each other, but they are several orders of magnitude smaller than the values previously reported in the literature for purely aqueous solutions. Moreover, K_H decreases with increasing water content. For PPh_3 at 1.0 M ionic strength ($\text{CF}_3\text{SO}_3\text{H} + \text{CF}_3\text{SO}_3\text{Li}$), the values of K_H are $24.0 \pm 0.8 \text{ M}^{-1}$ ($\text{CH}_3\text{CN}/\text{H}_2\text{O} = 90:10, \text{ v/v}$), 7.9 ± 0.7 (85:15), 4.2 ± 0.3 (80:20), 2.2 ± 0.1 (70:30), and 1.5 ± 0.3 (50:50). The binding of the proton is weaker at lower electrolyte concentrations, such that at $\mu = 0.40 \text{ M}$ in 90:10 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ K_H for PPh_3 is only $3.9 \pm 0.3 \text{ M}^{-1}$.

Introduction

Triarylphosphines and their ring-substituted derivatives are frequent substrates in studies of oxygen atom transfer. Such reactions generate triarylphosphine oxides, OPAr_3 , which do not readily exchange oxygen with standard solvents.¹ The transfer of isotopically labeled oxygen from a donor to PAr_3 therefore provides unequivocal demonstration of the mechanism. A number of kinetic studies of O atom transfer also have been carried out. The data obtained in that effort provide a useful reactivity scale that allows one to gauge the donor ability of potential new oxygen atom donors.

The majority of the work with triarylphosphines has been carried out in nonaqueous solvents, in part because of the requirements determined by a particular reaction, and in part because of the low solubility of PAr_3 in water. Nonetheless, aqueous and semiaqueous solvents have been used in several instances and will continue to be used in a world looking to replace organic solvents with water where possible. In the case of triarylphosphines, aqueous work is possible by employing water-soluble (sulfonated) phosphines^{9–17} or by use of low concentrations of phosphines in mixed aqueous/organic solvents.

Our recent work on O atom transfer from hydroperoxo metal complexes to PAr_3 in mixed $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ solvents^{18–20} was carried out in the presence of mineral acids that exhibited a strong catalytic effect, thought to arise from the much greater reactivity of the protonated hydroperoxide, eqs 1 and 2 ($\text{L}^1 = [\text{14}] \text{aneN}_4$, $\text{M} = \text{Cr}^{\text{III}}, \text{Rh}^{\text{III}}$). In all the cases studied, the acid dependence persisted even in strongly acidic solutions ($\text{pH} < 2$).



These results seem to contradict the current understanding of acid–base equilibria of phosphines. The $\text{p}K_a$ of triphenylphosphonium ion in water, originally reported by Streuli²¹ and routinely quoted in the literature,^{22–24} is 2.73. This value, which was obtained²¹ by extrapolation and manipulation of the data obtained in nonaqueous and semiaqueous solutions, requires that large proportions of the phosphine be present as unreactive phosphonium ions in strongly acidic solutions utilized in our work with hydroperoxides. In fact, the fraction of PPh_3 in that work would be even smaller than predicted by eq 3 because the protonation of the phosphine should be even more extensive in mixed $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ solvents than in pure water. Similar

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